RI 9488

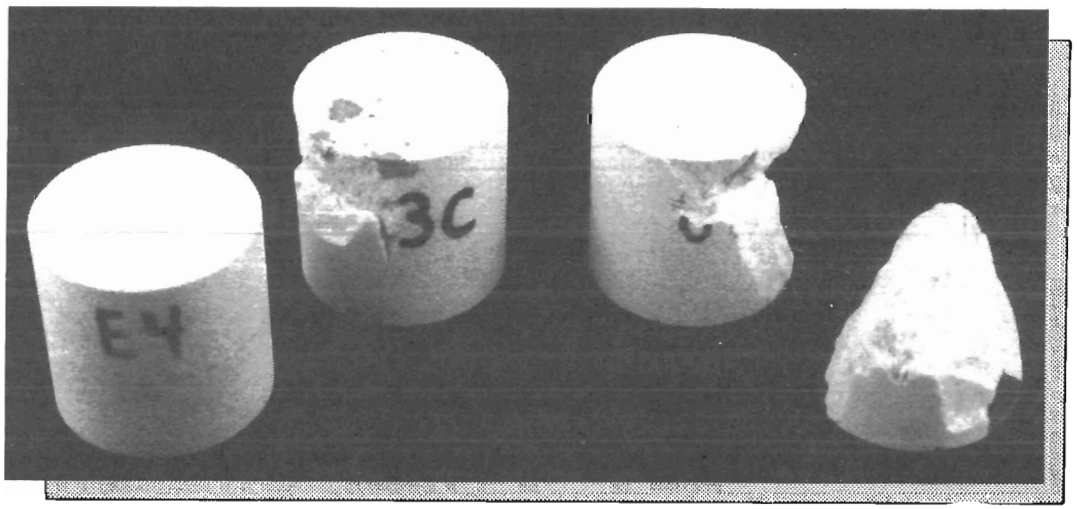
REPORT OF INVESTIGATIONS/1993



# Chemically Induced Strength Changes in Sandstone



By William P. Stroud and Dennis R. Dolinar




UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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*Cover Photograph: Sandstone specimens failed under uniaxial compression.*

Bureau of Mines
Report of Investigations 9488

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## ERRATA

Add the following text:

On page 2, at the end of the first paragraph under "Test Material, Saturation Fluids, and Zeta Potential":

> The siliceous nature of the sandstone cementation was confirmed by scanning electron microscopy and energy dispersive analysis.

On page 4, at the end of the second full paragraph:

> A fresh sample was used for each zero point of charge determination.

On page 4, at the end of the fourth full paragraph:

> Throughout this work, the assumption was made that the measurements made on crushed material accurately reflected the zeta potential of the intact sandstone cores.

On page 11, following the paragraph numbered "5":

> 6. The particular specimens selected for these experiments simply did not exhibit the effects observed by other researchers. Again, this seems highly unlikely.

International Standard Serial Number
ISSN 1066-5552

# CONTENTS



## ILLUSTRATIONS



## TABLES

## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

| | | | |
|---|---|---|---|
| cP | centipoise | min | minute |
| °F | degree Fahrenheit | mL/h | milliliter per hour |
| h | hour | mm | millimeter |
| in | inch | μm | micrometer |
| in•lbf | inch pound (force) | mol/L | mole per liter |
| L | liter | mV | millivolt |
| lb | pound | mV/mm | millivolt per millimeter |
| lb/in | pound per inch | ppm | part per million |
| L/min | liter per minute | psi | pound per square inch |
| m | meter | s | second |

# CHEMICALLY INDUCED STRENGTH CHANGES IN SANDSTONE

By William P. Stroud[1] and Dennis R. Dolinar[2]

## ABSTRACT

Chemical alteration of the compressive strength of sandstone has been investigated by the U.S. Bureau of Mines (USBM). Successful development of this technology would offer an attractive alternative to the methods now used for stress control in mines. Sandstone cores were stressed to failure under uniaxial compression at two different strain rates. Specimens saturated with either distilled or tap water showed an average 14% reduction in stress at failure compared with those dried in vacuum. Samples saturated with dilute solutions of aluminum chloride, hydrochloric acid, and polyethylene oxide showed no statistically significant difference in failure stress compared with those saturated with water. By contrast, compressive strength of the cores was increased some 7% by saturation with the nonpolar solvent carbon tetrachloride. No correlation was found between zeta potential and compressive strength.

[1]Physical scientist.
[2]Mining engineer.
Denver Research Center, U.S. Bureau of Mines, Denver, CO.

## INTRODUCTION

Bump-prone coal mine areas are destressed by auger drilling or blasting. Because these practices are both time consuming and expensive, many mining companies do not incorporate them into the extraction sequence. Studies have suggested (*1*),[3] however, that the strain energy of geologic materials could be substantially reduced by the injection of a suitable chemical surfactant, such as aluminum chloride. Development of chemical destressing techniques would provide an attractive alternative to conventional methods. The purpose of the research described in this U.S. Bureau of Mines (USBM) report was to evaluate the feasibility of chemically reducing the compressive strength of coal mine rock. This work was done in support of a USBM program to reduce mine accidents caused by ground failure. Specific goals were to determine (1) whether or not the compressive strength of the rock was affected by saturation with any one of a number of test fluids, and (2) whether or not the compressive strength of the saturated rock was affected by the zeta potential of the system.

In 1944 Rehbinder (*2*) described the "chemomechanical weakening" of rock. Since that time, researchers have continued to report changes in the mechanical properties of geologic materials saturated with certain fluids. Changes in yield stress (*3-10*), crack propagation rate (*11*), fracture toughness (*12*), surface hardness (*13*), and drilling rates (*14-16*) have all been observed. Numerous mechanisms have been proposed to explain these effects. Rehbinder suggested that adsorption of a saturating fluid resulted in a change in the surface free energy of a developing crack. In a second model proposed by Westwood (*17*), dislocation density at the crack tip was modified by the zeta potential existing between the surfactant and the rock surface. Other researchers extended the theory of stress corrosion cracking to geologic materials (*18-19*). Because of the continuing controversy surrounding experimental results, none of these models can be either confirmed or precluded at present.

## ACKNOWLEDGMENTS

Michael Harmel, geophysicist, Denver Research Center (DRC), USBM, was responsible for the careful preparation of the samples prior to testing. Ronald Gerlick, engineering technician, DRC, conducted all mechanical testing of the samples.

## EXPERIMENTAL DESIGN

### TEST MATERIAL, SATURATION FLUIDS, AND ZETA POTENTIAL

Siliceous sandstone was chosen as a test material partly because of its widespread geologic occurrence and association with coal mine bumps and bursts, and also because several researchers have proposed mechanisms involving Si-O bonds (*9, 20*). Accordingly, NX cores of this material were prepared for uniaxial compression testing. Specific gravity and apparent porosity of the finished specimens were 2.36% and 10.0%, respectively.

A major disadvantage in using a naturally occurring material is the variability in its physical properties, either laterally over the bedding plane, or vertically in the core column. Because of this variability, a relatively large number of samples was used for the data base. Similarly, samples were randomly chosen from the core column in an attempt to reduce any systematic bias. Other researchers have avoided these difficulties by using more homogeneous materials such as synthetic quartz (*3*).

Saturating fluids were chosen from those most commonly reported in the literature as being used in similar experiments. Aluminum chloride has been found to reduce compressive strength in geologic materials (*9*). Polyethylene oxide was chosen primarily because of the increased drilling rates reported by the USBM's Twin Cities Research Center (TCRC) using this polymer (*16*). Dilute hydrochloric acid was used to modify both the pH and the zeta potential of the solutions. Finally, carbon tetrachloride was chosen as a saturating fluid because of its nonpolar nature, as opposed to water, aluminum chloride, and hydrochloric acid. An added advantage of using carbon tetrachloride is that its viscosity is the same as that of water.

When a solid is immersed in a liquid electrolyte, ions from the solution are adsorbed onto the surface. Counterions of opposite charge are then attracted to these ions, forming a so-called "double layer" (fig. 1). If a flow is

[3]Italic numbers in parentheses refer to items in the list of references at the end of this report.

established, the surface of shear is approximately coincident with the monolayer of adsorbed ions on the mineral surface. As shown in figure 2, the potential between the surface of shear and an infinitely distant point in the solution is called the zeta potential (*21-22*).

Much has been written regarding the role of the zeta potential in the chemical weakening of rock materials. Researchers have variously correlated minimum compressive strength with zero zeta potential (*6*), minimum drilling energy with zero zeta potential (*15-16*), and minimum compressive strength with maximum positive zeta potential (*9*). For this reason, it was decided to measure the zeta potential of the sandstone in all saturating solutions used in the experiments.

## MEASUREMENT OF ZETA POTENTIAL

A major part of the research effort entailed design and construction of an apparatus to measure the zeta potential of sandstone samples in solution. Fluid motion relative to a solid phase will result in displacement of the electrical double layer, resulting in a net potential difference. If a colloidal solid phase is mobile in the fluid under the influence of an electric field, the phenomenon is known as electrophoresis. The electrophoretic method is the basis for a number of commercial instruments designed to measure zeta potential. If, on the other hand, the fluid is in motion relative to a stationary solid phase, the resulting electromotive force (emf) is referred to as a "streaming potential." This latter method was chosen to measure zeta potential.

The Helmholtz-Smoluchowski equation may be used to relate streaming potential to zeta potential (*22*, p. 763).

$$\zeta = \frac{\eta \sigma V}{\epsilon P},$$

where $\zeta$ = zeta potential,

$\eta$ = fluid viscosity,

$\sigma$ = fluid conductivity,

$\epsilon$ = dielectric constant of the fluid,

V = streaming potential,

and P = pressure differential driving the fluid.

If there is no potential offset in the system, i.e., if the streaming potential is zero at zero pressure, absolute values of V and P can be used in this calculation. If a potential offset does exist, zeta can still be calculated from the relationship

$$\zeta = \frac{\eta \sigma \Delta V}{\epsilon \Delta P},$$

where $\Delta V$ and $\Delta P$ represent the differences in streaming potential and pressure, respectively, in successive measurements. The ratio $\Delta V$-$\Delta P$ is frequently referred to as the "coupling coefficient."

Figure 3 shows the design of the streaming potential cell used in this work. The cell is constructed from commercially available 1/2-in polyvinyl chloride (PVC) pipe

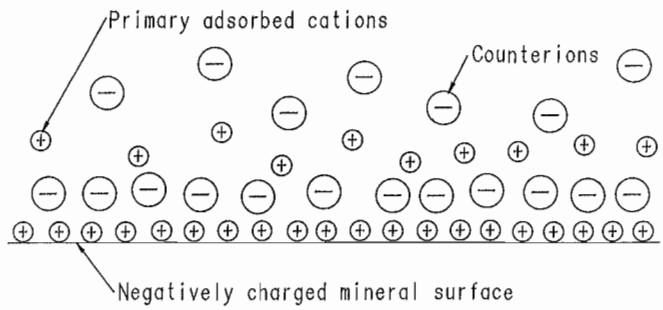


**Figure 1.—Simplified model of electrical double layer.**

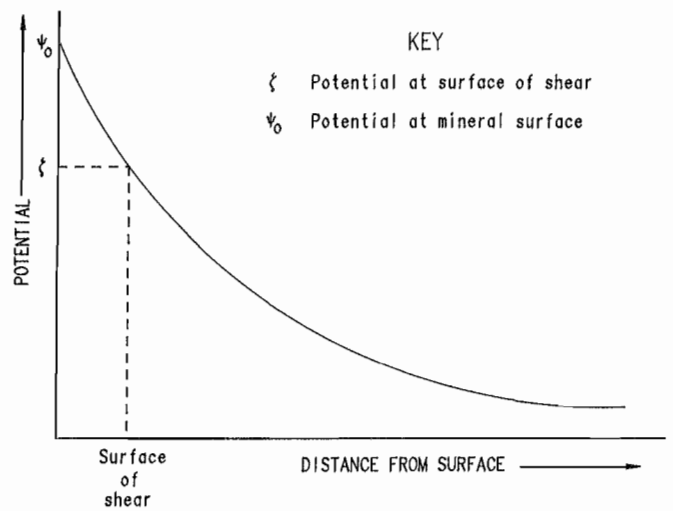


**Figure 2.—Zeta potential schematic.**

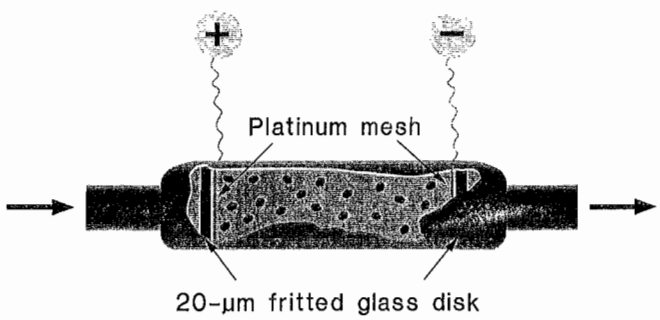


**Figure 3.—Streaming potential cell design.**

fittings. The crushed sample material is held in place by 20-$\mu$m fritted glass discs. Platinum gauze is used for the internal electrodes. Streaming potentials were measured on a digital electrometer readable to 0.01 mV. All calculations for aqueous solutions assumed a relative dielectric constant of 79 and a viscosity of 0.90 cP. Solution conductivity was measured on a digital conductivity meter accurate to ±0.3% at full scale.

A 10-L solution reservoir is connected to the cell by vinyl tubing, and is positioned approximately 1 m above the cell. The measured height of the solution in the reservoir can be directly converted to hydrostatic pressure in appropriate units. The column height can be easily measured with a precision of 1 mm, affording a high precision in the determination of $\Delta P$. This method is basically the "staircase" procedure described by Morgan (*23*).

For each series of zeta potential measurements, samples from several sandstone cores were crushed, mixed, and screened. The fraction -12 to +16 mesh was taken as a composite sample representing average properties of all the core. The composite sample was then loaded into the streaming potential cell and the solution allowed to flow through the cell. A flow rate of 40 mL/h was typical for a 1,000-mm pressure head.

Equilibrium was determined when no further change in the measured streaming potential was noted over a 4-h period. This value was recorded and the fluid reservoir moved to a different height. The system was tested for linearity by recording V and P for five successive measurements. Regression analysis of the data showed the plot to be linear with a 0.999 correlation coefficient. Typical coupling coefficient values were on the order of $10^{-2}$ mV/mm.

An attempt was made to compare values for zeta potential determined in the streaming potential cell with those measured electrophoretically for the same material. Researchers at TCRC had previously measured the zeta potential of Sioux quartzite in Minneapolis tap water using a commercial electrophoretic instrument (*24*). Reported values for zeta ranged from -29 to -44 mV. TCRC provided samples of the same material for this comparison. The average value of zeta for the same material in Denver tap water determined by the streaming potential method was -33 mV. Good agreement is seen between the two methods.

## SPECIMEN PREPARATION

Specimens were obtained from 10- to 12-in-long cores drilled from a sandstone block. Nominal diameter of the cores was 2.125 in. Samples were cut to the desired length with a diamond saw using water as a coolant and then surface finished with a grinder to a flatness of ±0.002 in. The finished specimen length was 2.125 in with a tolerance of 0.025 in, giving a sample aspect ratio of 1.

## VACUUM SATURATION

Broch (*10*) related the uniaxial compressive strengths of several materials to their degree of water saturation. For this reason, it was decided that specimens used in the USBM tests would be outgassed in a vacuum followed by fluid saturation in the vacuum chamber. The interiors of the failed cores were found to be wet, indicating effective saturation of the samples.

The vacuum saturation apparatus consisted of a 25-L/min, two-stage mechanical pump and a bell jar. A 9-in-diam naval brass plate served as a base. Brass was chosen for all valves and fittings used in the system to minimize corrosion. A removable glass foreline trap immersed in a dry ice-alcohol slurry prevented moisture from reaching the pump. This trap was necessary since water was used in the initial cutting of the core specimens. The empty system routinely produced pressures less than $1 \times 10^{-3}$ torr.

In practice, 10 of the finished sandstone samples were loaded into a stainless steel vessel, which was in turn placed under the bell jar. Normally, the system would reach a 10-$\mu$m vacuum within 24 to 36 h, depending upon the amount of water absorbed by the sample during preparation. When a satisfactory vacuum was attained, the main valve was closed, isolating the vacuum pump from the bell jar. A second valve was then opened, allowing the saturating solution under atmospheric pressure to fill the steel container. When sufficient solution had been admitted to cover the core specimens, the second valve was closed. The saturating fluid was then permitted to outgas under partial vacuum until all evolution of gasses had ceased. At that time, the system was vented to atmospheric pressure and the stainless steel vessel containing the samples and the fluid removed. Finally, the container was sealed to minimize diffusion of air into the fluid. Core samples were kept in the saturating fluid until time of mechanical testing. In the special case where samples were vacuum dried only and not saturated, the specimens were removed from the vacuum chamber, wrapped in plastic to minimize any absorption of atmospheric moisture, and tested in air. During the experiments, the ambient laboratory atmosphere was maintained at a relative humidity of less than 10% and a temperature of 70° F.

## MECHANICAL TESTING

Mechanical testing of all samples was done under uniaxial compression on a stiff, closed-loop, servo-controlled hydraulic press with a rated capacity of 600,000 lb. All tests were conducted under stroke control with a constant

displacement rate applied to the sample. Axial and lateral deformation of specimens were measured by linear variable differential transducers. Typical axial deformation for the 2.125-in cores was on the order of $1.2 \times 10^{-2}$ in. In consideration of the possibility that any effect of the chemical environment might be dependent on strain rate, tests were conducted at two different strain rates of approximately $1 \times 10^{-5}$ $s^{-1}$ and $1 \times 10^{-6}$ $s^{-1}$.

Since the former tests lasted only about 10 min, samples were taken directly from the saturating fluid and placed in the press. Specimens tested at the lower strain rate were wrapped in plastic to prevent any evaporation of the saturating fluid during the 100-min duration of this test. In most tests, a sharp inflection in the load curve was coincident with the visible failure of the sample.

## RESULTS

Table 1 lists the results of the compressive strength tests. The Student's t test was used to determine if the test results were significantly different from the mean of the reference population. Table values for t were based on a 99% confidence interval, and assumed a two-tailed distribution with N-1 degrees of freedom. The observed value of t was calculated assuming that only estimates of the two means were available.

The problem of variability in geologic materials has already been noted. For this reason, it was felt that 25 vacuum-dried samples were the minimum number necessary to form an adequate data base.

**Table 1.—Results of uniaxial compression tests of sandstone cores, dried and vacuum saturated**

| Test description | Number of samples | Failure stress, psi | | Zeta, mV | Student's t | | Comment |
|---|---|---|---|---|---|---|---|
| | | Mean | SD | | Table | Calc | |
| STRAIN RATE, $1 \times 10^{-5}$ $s^{-1}$ | | | | | | | |
| Vacuum dried | 25 | 27,302 | 1,753 | NAp | NAp | NAp | Reference base. |
| Vacuum saturated, water only: | | | | | | | |
| Tap water | 20 | 23,554 | 1,587 | -21 | 2.69 | 7.43 | 14% reduction in stress at failure, compared with vacuum-dried samples. |
| Distilled water | 10 | 24,015 | 1,963 | -36 | 2.76 | .69 | No significant difference in failure stress, compared with tap-water-saturated samples. |
| Vacuum saturated, water with HCl: pH 1.9 HCl, tap water estimated to be at ZPC. | 10 | 24,028 | 1,185 | 0 | 2.76 | .83 | Do. |
| Vacuum saturated, water with $AlCl_3$: | | | | | | | |
| p[$AlCl_3$] 4.87, tap water estimated to be at ZPC. | 13 | 22,836 | 2,375 | 0 | 2.75 | 1.04 | Do. |
| p[$AlCl_3$] 2.0, tap water | 5 | 24,598 | 1,167 | +37 | 2.81 | 1.37 | Do. |
| p[$AlCl_3$] 3.0, tap water estimated to be at maximum zeta potential. | 10 | 21,985 | 2,141 | +47 | 2.76 | 2.27 | Do. |
| p[$AlCl_3$] 4.0, tap water | 10 | 24,193 | 1,322 | +22 | 2.76 | 1.09 | Do. |
| p[$AlCl_3$] 5.0, tap water | 5 | 23,315 | 1,588 | -03 | 2.81 | .30 | Do. |
| Vacuum saturated, water with PEO: | | | | | | | |
| 100,000-mol-wt PEO, 20 ppm, tap water. | 10 | 23,703 | 2,183 | +08 | 2.76 | .20 | Do. |
| 5,000,000-mol-wt PEO, 20 ppm, tap water. | 9 | 24,152 | 1,794 | ND | 2.77 | .90 | Do. |
| Vacuum saturated, $CCl_4$ | 10 | 29,183 | 1,226 | ND | 2.75 | 3.09 | Statistically significant difference in failure stress, compared with vacuum-dried samples. |
| STRAIN RATE, $1 \times 10^{-6}$ $s^{-1}$ | | | | | | | |
| Vacuum dried | 10 | 26,205 | 1,157 | ND | 2.75 | 1.82 | No significant difference in failure stress, compared with vacuum-dried samples that failed at higher strain rate. |
| Vacuum saturated, tap water | 10 | 22,913 | 1,082 | -21 | 2.76 | 1.15 | Do. |
| Vacuum saturated, water with $AlCl_3$: | | | | | | | |
| p[$AlCl_3$] 3.0, tap water estimated to be at maximum zeta potential. | 10 | 22,524 | 1,624 | +47 | 2.76 | 1.66 | Do. |

NAp Not applicable.
ND Not determined.
SD Standard deviation.

Samples in the first comparison group were vacuum saturated with tap water as previously described. Mean failure stress was determined to be 23,554 psi, or approximately a 14% reduction in mean failure stress compared with the vacuum-dried cores. This set saturated with tap water became, in turn, the reference base with which all subsequent saturated core tests were compared.

Prior analysis of Denver tap water had shown some 14 ppm calcium to be present (*24*, p. 17). To evaluate any possible effects of this or other extraneous ions on compressive strength, 10 samples were saturated with commercial distilled water. Mean failure stress for this group was 24,015 psi, virtually the same as that reported for samples saturated with tap water.

As previously discussed, researchers disagree as to the role of the zeta potential in altering mechanical properties of rock materials. Some investigators such as Swolfs (*9*) have adduced mechanisms involving particular chemical species such as hydrous oxides. Ishido and Nishizawa (*7*) concluded that pH was a major factor in determining the zeta potential of mineral-water systems, and by inference, related to the crack growth rate.

In general, the ability of a specific ion to produce a zero point of charge (ZPC) condition is related to both the charge and size of that ion. For monovalent cations, the ability to effect ZPC, or critical flocculating power, is found experimentally to follow the series $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ (*22*, pp. 720-722). The rationale for this effect is seen in the lower charge density and resulting greater polarizibility of the larger ions. Ions with greater induced dipole moments are more strongly adsorbed on the mineral surface. The relation of ionic charge to flocculating power is complex, but in general is a function of the sixth power of the charge (*22*, p. 720).

An experiment was devised to differentiate between mechanisms involving hydrous oxides, such as $Al(OH)_3$ and $Fe(OH)_3$, and effects related solely to zeta potential. Addition of dilute hydrochloric acid was used to effect a zero zeta potential or ZPC. This was determined to occur in the tap water-sandstone system at a pH of 1.9. This value compares well with the ZPC of pH 2.0 reported by Ishido and Mizutani (*6*) for a quartz-nitric acid system. Additional data points, as shown in figure 4, produced a curve closely paralleling their results, but shifted to the acid region by about 0.1 pH unit.

Accordingly, 10 cores were vacuum saturated with a tap water-hydrochloric acid solution at pH 1.9. Mean failure stress for the group was 24,028 psi. Again, no significant difference was noted compared with those samples saturated with tap water only. It was concluded that a zero zeta potential condition obtained with $H^+$ as the potential determining ion did not affect the compressive strength of the sandstone specimens.

A solution of aluminum chloride in tap water was chosen as the saturating fluid in the next series of experiments. There were several reasons for this choice. Flocculating power, as previously discussed, is a function of the sixth power of the charge on the ion added to the system. As a consequence, $Al^{+3}$ is almost three orders of magnitude more effective in this role than a monovalent ion. Since most minerals exhibit a substantially negative zeta potential in neutral water, the $Al^{+3}$ ion has been used extensively to attain a ZPC condition with various minerals (*6-7, 24*). Ishido and Mizutani reported that the minimum compressive strength of quartz diorite occurred at ZPC in an aluminum nitrate solution (*6*). Finally, aluminum chloride was chosen rather than aluminum nitrate to allow direct comparison with the work of Swolfs (*9*).

ZPC of the composite sandstone sample was determined by streaming potential measurements to occur at a concentration of $1.4 \times 10^{-5}M$ aluminum chloride in tap water (fig. 5). Watson and Tuzinski (*24*) reported a ZPC concentration of $1.2 \times 10^{-4}M$ aluminum chloride for a Sioux quartzite-tap water system. It should be noted that

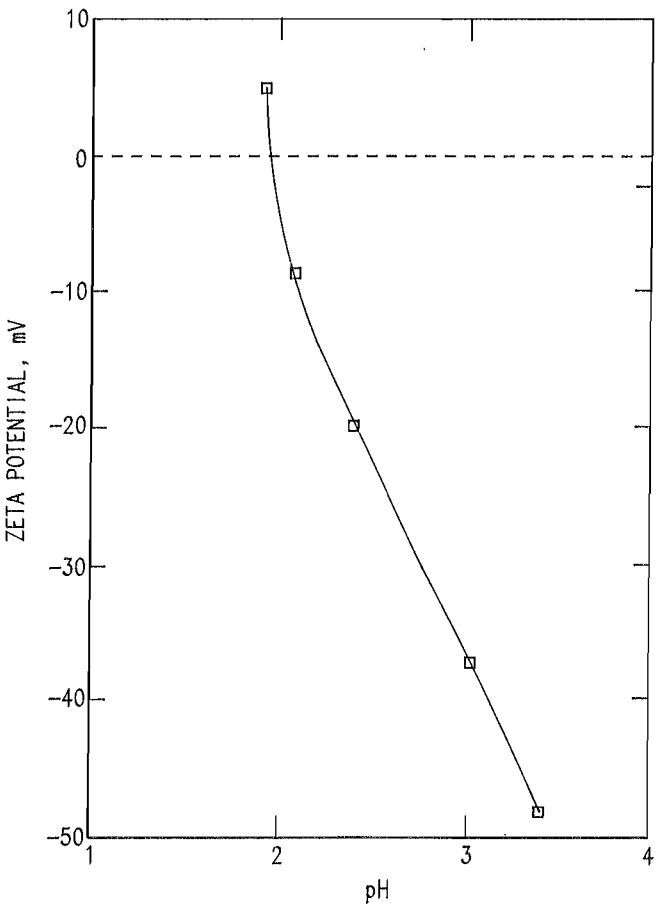


**Figure 4.—Zeta potential plot—hydrochloric acid.**

in both these experiments the aluminum chloride solution was maintained at a pH of 4.0 by the addition of hydrochloric acid, in order to prevent the precipitation of aluminum hydroxide.

$$[Al(OH)_3] = [Al^{+3}]\,[OH^-]^3 \qquad K_{sp} = 5 \times 10^{-33}.$$

It is important that this distinction be made, since proposed mechanisms have entailed $Al^{+3}$ and $Al(OH)_3$ as well as other related species. As seen in table 1, 13 specimens were vacuum saturated with a $1.4 \times 10^{-5}M$ solution of aluminum chloride, maintained at pH 4.0 by the addition of hydrochloric acid. No statistically significant reduction in mean failure stress was observed.

In a paper written in 1972, Swolfs (*9*) reported a 15% reduction in the compressive strength of Coconino sandstone saturated with an aluminum chloride solution, compared with specimens saturated with distilled deionized water. Swolfs' contention was that the greatest reduction in compressive strength corresponded not to ZPC, but to maximum positive values of zeta potential. The high zeta potential was regarded as an indication of maximum adsorption of hydrous oxides and other related species that Swolfs believed to be responsible for weakening Si-O bonds in the sandstone matrix.

In order to test Swolfs' hypothesis, sandstone cores were vacuum saturated with aluminum chloride in tap water at concentrations of $10^{-2}$, $10^{-3}$, $10^{-4}$, and $10^{-5}$ mol/L. In this case no attempt was made to control the pH of the solutions. Five specimens were saturated at each concentration. Researchers at TCRC indicated that the maximum observed zeta potential of Sioux quartzite in aluminum chloride was about +40 to +60 mV (*25*). Streaming potential tests in this laboratory conducted on composite sandstone in $10^{-3}M$ aluminum chloride in tap water showed a maximum zeta potential of +47 mV, consistent with the TCRC results. Uniaxial compression tests of samples vacuum saturated with $10^{-2}M$, $10^{-3}M$, $10^{-4}M$, and $10^{-5}M$ aluminum chloride showed no statistically significant reduction in compressive strength relative to samples saturated with tap water only.

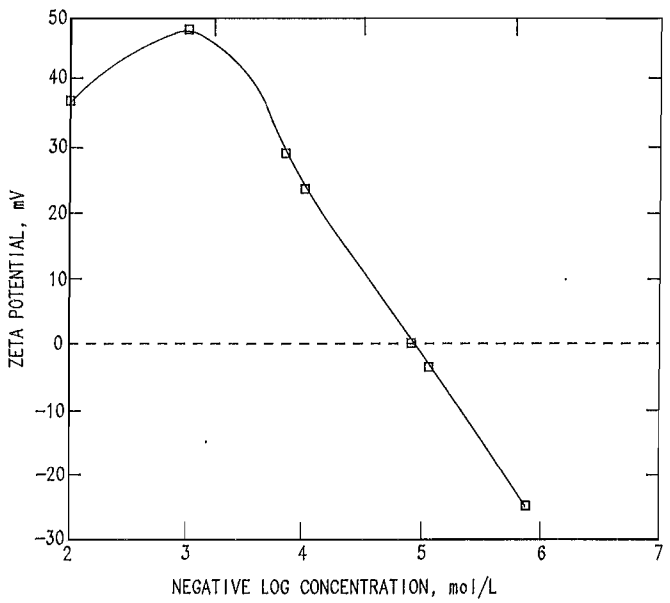


**Figure 5.—Zeta potential plot—aluminum chloride.**

Polyethylene oxide, or PEO, is a long-chain water-soluble polymer with the basic structural unit $-CH_2CH_2O-$. Polymers of this type have long been used in the steric stabilization of colloidal dispersions (*22*). Researchers at TCRC had reported that the addition of PEO to rock-water systems produced a ZPC condition (*16, 24*). The unique feature of this effect was that ZPC was approached asymptotically with increasing concentrations of PEO, and that above a certain threshold concentration (generally about 10 ppm), zeta potential remained zero, even with further additions of the polymer. TCRC researchers also reported substantial increases in penetration rate and bit life in laboratory drilling tests of Sioux quartzite maintained at ZPC with the polymer solution.

Douglas and Dunning,[4] on the other hand, did not observe asymptotic behavior when measuring the zeta potential of synthetic quartz in PEO. Similarly, they reported that the addition of PEO did not change the failure stress of synthetic quartz under diametral compression, relative to the same material in distilled, deionized water. Given this background, it was decided to use PEO as a saturating fluid in this laboratory's sandstone tests.

Streaming potential measurements were made to determine the zeta potential of composite sandstone in 100,000-mol-wt PEO. Tests were conducted from 0 to 100 ppm. Figure 6 shows the results of this experiment. Over this concentration range zeta rose sharply from -21 mV for untreated tap water to a maximum of +23 mV at 10 ppm PEO. Further additions of polymer resulted in a slow decrease in potential to +7 mV at 25 ppm. Zeta potential then remained constant at +7 mV from 25 to 100 ppm. No evidence was seen of a stable ZPC. These results bear some similarity to those reported by Douglas and Dunning for synthetic quartz in PEO, but are totally contrary to those reported by TCRC.

It is significant that the emf produced by the streaming potential cell using the PEO solution was irreversible; replacement of the polymer solution with tap water did not significantly change the observed potential. This result strongly suggests that PEO, even in low concentrations, effectively coats the cell electrodes and rock surfaces.

[4]Douglas, B., and J. Dunning. Single Crystal Studies of the Role of Electrostatic Potential and PZC in Chemical Weakening. Draft summary report, BuMines contract C00290004, Nov. 1990; available from P. A. Tuzinski, BuMines, Minneapolis, MN.

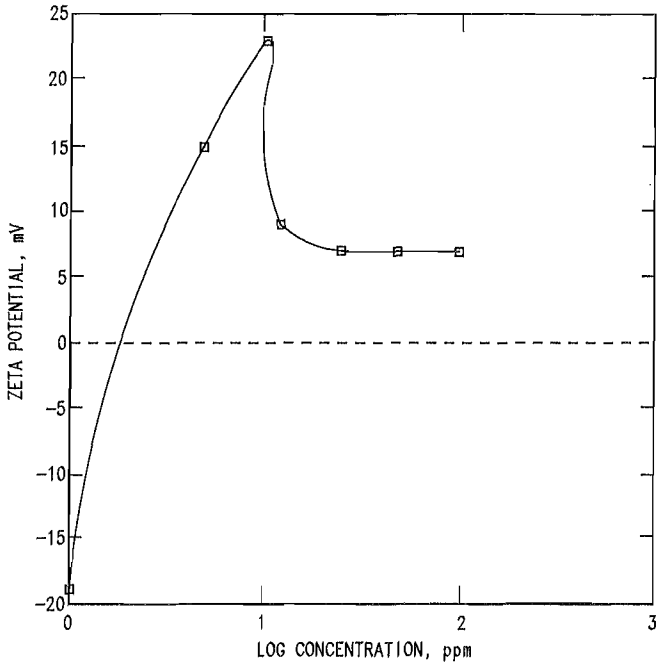


**Figure 6.—Zeta potential plot—100,000-mol-wt polyethylene oxide.**

Such behavior is consistent with that described in the literature for this polymer.

Since no asymptotic ZPC was found for the sandstone-PEO system, an arbitrary concentration of 20 ppm was chosen. Samples were saturated with both 100,000- and 5-million-mol-wt PEO. Again, no significant difference in failure stress was observed in samples saturated with either molecular weight.

In order to investigate the possible effects of strain rate on failure stress, duration of the uniaxial compression tests was lengthened to approximately 2 h, resulting in a new strain rate of $1 \times 10^{-6}$ $s^{-1}$. To establish a new reference base at the lower strain rate, 10 vacuum-dried specimens were stressed to failure. Mean failure stress for these cores was 26,205 psi. The Student's t test showed no significant difference in failure stress compared with vacuum-dried samples failed at the higher strain rate.

Ten samples vacuum saturated with tap water were also tested at the $1 \times 10^{-6}$ $s^{-1}$ strain rate. Mean failure stress for this group did not differ significantly from that reported for water-saturated samples failed at the higher strain rate.

Personal conversations with other researchers had suggested that any chemical destressing effect present would be enhanced by a lower strain rate (*26*). For this reason, samples were saturated with the only fluid that had shown any possibly enhanced weakening effect relative to the water-saturated samples, i.e., $10^{-3}$ mol/L aluminum chloride in tap water. No statistically significant difference in the mean failure stress was noted between these specimens and those failed at the higher strain rate.

All previous tests had been conducted in aqueous solutions. Water itself is unique in many respects, i.e., large dipole moment, high dielectric constant, etc. It is also one of the few substances capable of forming hydrogen bonds. For the next series of tests it was decided to use a test fluid markedly different from water. Carbon tetrachloride was chosen as a saturating fluid because of its nonpolar nature and low dielectric constant. On the other hand, the carbon tetrachloride and water molecules are similar in size. Viscosities for the two liquids are essentially the same.

Mean failure stress for the 10 samples saturated with carbon tetrachloride was 29,183 psi, with a standard deviation of 1,226 psi. The 29,183-psi figure represents an increase of approximately 7% over the mean failure stress for the vacuum-dried cores. Results of the t test showed this difference to be statistically significant at the 99% confidence level.

Although the measurement of failure stress is emphasized in this report, strain energy is also of paramount importance. The strain energy required to deform and fail a specimen can be determined by measuring the area under the load deformation curve. Table 2 shows the strain energy at failure for dried and vacuum-saturated core specimens. For both strain rates, there were statistically significant reductions of 15% and 14% in the strain energy of the water-saturated samples relative to the vacuum-dried samples. Specimens saturated with $10^{-3}M$ aluminum chloride and tested at the lower strain rate also showed a decrease in strain energy of some 8% relative to the water-saturated samples. This result, however, was not statistically significant. When PEO of either molecular weight was used as the saturating fluid, there was no statistically significant difference in strain energy relative to the water-saturated samples. Specimens saturated with carbon tetrachloride showed a statistically significant 20% increase in strain energy relative to vacuum-dried cores.

In addition to reductions in the compressive strength and strain energy, stiffness of the water-saturated specimens was also reduced relative to that of the vacuum-dried samples. Figure 7 shows the average load-deformation curves for the first three groups of samples listed in table 2. In these tests, vacuum-dried specimens, specimens saturated with tap water, and specimens saturated with carbon tetrachloride were loaded at a strain rate of $1 \times 10^{-6}$ $s^{-1}$. For any given load, the water-saturated specimens showed a greater displacement than those that had

been vacuum dried. The greatest change in displacement difference occurred at the lower load levels. Displacement difference between the vacuum-dried and the water-saturated samples was $2.0 \times 10^{-4}$ in at 2,000 lb, $4.3 \times 10^{-4}$ in at 8,000 lb, $4.4 \times 10^{-4}$ in at 10,000 lb, and $5.1 \times 10^{-4}$ in at 40,000 lb. Beyond 10,000 lb there was only a small increase in the displacement difference between the two sample groups. The average stiffness from 0 to 2,000 lb was 2.5 million lb/in for the vacuum-dried samples and 2 million lb/in for those saturated with tap water. From 30,000 to 40,000 lb the average stiffness was 8.24 million lb/in for the vacuum-dried samples, and 7.98 million lb/in for the water-saturated samples. At the lower load level, the stiffness was reduced by approximately 20%, while at the higher load the stiffness has been reduced by only 3%. This is a further indication that the stiffness properties of the sandstone are most affected at the lower loads. There is little difference in the load-deformation curves for the vacuum-dried and carbon tetrachloride-saturated specimens until the onset of fracturing in the vacuum-dried samples.

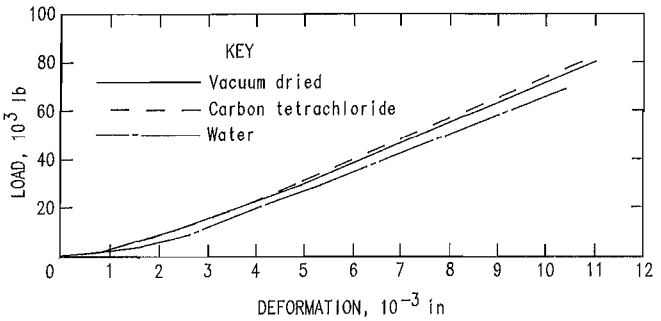


**Figure 7.—Load deformation curves for selected sandstone specimens.**

**Table 2.—Strain energy at failure of sandstone cores, dried and vacuum saturated**

| Test description | Number of samples | Strain energy, in•lbf | | Student's t | | Comment |
|---|---|---|---|---|---|---|
| | | Mean | SD | Table | Calc | |
| STRAIN RATE, $1 \times 10^{-5}$ $s^{-1}$ | | | | | | |
| Vacuum dried | 5 | 549 | 33 | NAp | NAp | Reference base. |
| Vacuum saturated, $CCl_4$ | 10 | 658 | 59 | 3.01 | 3.80 | 20% increase in strain energy, compared with vacuum-dried samples. |
| Vacuum saturated, tap water | 10 | 468 | 41 | 3.01 | 3.82 | 15% decrease in strain energy, compared with vacuum-dried samples. |
| Vacuum saturated, water with PEO: 200,000-mol-wt PEO, 20 ppm, tap water | 10 | 450 | 43 | 2.88 | .96 | No significant difference in strain energy, compared with tap-water-saturated samples. |
| 5,000,000-mol-wt PEO, 20 ppm, tap water | 9 | 468 | 41 | 2.89 | .00 | Do. |
| STRAIN RATE, $1 \times 10^{-6}$ $s^{-1}$ | | | | | | |
| Vacuum dried | 10 | 517 | 42 | NAp | NAp | Reference base. |
| Vacuum saturated, tap water | 10 | 447 | 28 | 2.88 | 4.38 | 14% decrease in strain energy, compared with vacuum-dried samples. |
| Vacuum saturated, water with $AlCl_3$: p[$AlCl_3$] 3.0, tap water estimated to be at maximum zeta potential. | 10 | 410 | 48 | 2.88 | 2.11 | No significant difference in strain energy, compared with tap-water-saturated samples. |

NAp Not applicable.
SD Standard deviation.

## DISCUSSION

At the start of this investigation, it was recognized that several different mechanisms had been proposed over the years to explain the observed reduction in mechanical strength of rock materials saturated with various fluids. As noted previously, the purpose of the current investigation was to establish which, if any, of these mechanisms was valid, and to maximize the effect for use in mining applications. Because of the work reported by TCRC and others, the initial hypothesis in this investigation was that the greatest reduction in compressive strength would occur at ZPC, i.e., that fluid concentration at which the zeta potential is zero. This study produced no experimental evidence supporting that hypothesis.

A great deal of controversy has attended the question of just which chemical species are responsible for the reported changes in mechanical properties. However, it was impossible to differentiate between effects produced by $H^+$ and those produced by $Al^{+3}$ since specimens maintained at ZPC with either ion showed no significant change in failure stress. ZPC was determined to occur at a pH of 1.9 in a sandstone-hydrochloric acid system. This value agreed well with that reported by Ishido and Mizutani (*6*) for a quartz-nitric acid system. In the aluminum chloride experiments, ZPC was found to occur at a concentration of $1.4 \times 10^{-5}$ mol/L, again a value in good agreement with that reported by other workers using similar silicate minerals (*24*, p. 9). Gross error in determination of ZPC, then, would seem unlikely. Moreover, if chemical stress reduction occurs only at the exact point of zero zeta potential, the effect has no engineering application, since the smallest change in pH or solution composition would alter this value.

Work done in this laboratory with PEO did not confirm the asymptotic ZPC behavior reported by TCRC. A possible reason for this disagreement is a basic difference between the electrophoretic and streaming potential methods of measuring zeta potential. Successful determination of zeta using the electrophoretic method requires that the solid phase be present as very fine particles. Bridging or coagulation of the particles by long-chain polymers would greatly reduce their mobility in a field, leading to an incorrect estimate of zeta potential. Similarly, the use of an insufficiently high electrical field is a possible source of error in these measurements. Streaming potential measurements, on the other hand, would not be subject to this difficulty, because of the stationary nature of the relatively large rock particles used.

On the other hand, the 20-ppm concentrations of PEO should have produced a ZPC condition based on the TCRC work. Again, no significant difference in failure stress compared with the water-saturated samples was seen.

There are a number of similarities between this study and the work done by Swolfs. In both cases a siliceous sandstone was stressed to failure under uniaxial compression. Both used test specimens saturated with aluminum chloride at concentrations of $10^{-2}$, $10^{-3}$, $10^{-4}$, and $10^{-5}$ mol/L. No attempt was made to control pH, since Swolfs believed that the species formed by hydrolysis of the $Al^{+3}$ ion were responsible for the reduction in compressive strength reported in his work. Two differences are noted. Swolfs used distilled water, whereas solutions used in the present work were made from tap water. Similarly, the strain rate in Swolfs' work was $2 \times 10^{-4}$ $s^{-1}$ versus $1 \times 10^{-5}$ $s^{-1}$ and $1 \times 10^{-6}$ $s^{-1}$ used in this study.

Swolfs reported that samples saturated with distilled water failed at an average stress some 8% lower than those tested dry. The results presented in this report, however, show a 14% reduction in all samples saturated with aqueous solutions. Swolfs, on the other hand, reported an additional 15% reduction for those samples saturated with an aluminum chloride solution producing what he believed to be the maximum positive zeta potential. The greatest stress reduction in his work, then, was some 22% lower compared with vacuum-dried samples, not entirely dissimilar from the 14% found in this study. The problematic nature of the results at point of maximum positive zeta potential has already been discussed in the preceding section.

Unfortunately, Swolfs did not personally determine the maximum positive zeta potential for Coconino sandstone in aluminum chloride. He instead relied on data reported by Gaudin and Fuerstenau (*27*) for crushed quartz in an aluminum nitrate solution. Use of these data assumes that the presence of different anions had no effect on zeta potential, and that the surface chemistries of the crushed quartz and the Coconino sandstone were similar. Certainly, the presence of any nonquartzitic minerals in the Coconino sandstone could invalidate the latter assumption. The maximum positive zeta potential reported by Gaudin and Fuerstenau for crushed quartz occurred at an aluminum nitrate concentration of approximately $3 \times 10^{-5}$ mol/L. On the other hand, the sandstone-aluminum chloride system used in the present experiments showed a maximum positive zeta potential occurring at a concentration of $10^{-3}M$. Since this latter value is in good agreement with the maximum reported by Douglas and Dunning[5] for a synthetic quartz-aluminum chloride system, the question of anion effects remains problematical.

As previously noted, mean compressive stress at failure for the 10 samples vacuum saturated with carbon tetrachloride was 29,183 psi. This represents an increase of

[5]See footnote 4.

some 7% over the mean failure stress for the vacuum-dried cores. The Student's t test showed this finding to be statistically significant at both the 95% and 99% confidence levels.

A possible explanation for this result entails the exclusion of water from the carbon tetrachloride-saturated specimens. Wiederhorn (*28*) found both the crack velocity and strength dependence of glass to be related to the relative humidity of the ambient atmosphere. In the USBM experiments, the vacuum-dried specimens were exposed to the laboratory atmosphere for a brief period of time prior to and during mechanical testing. Small amounts of moisture could have been absorbed during that time. Conversely, the core samples saturated with carbon tetrachloride would not be affected in this way. A similar mechanism was suggested by Kuznetsov (*29*, p. 274) to explain the apparent increase in surface energy of mineral surfaces wetted by nonpolar liquids.

It is appropriate at this point to address the question of why this study did not show the chemical weakening effects reported by other researchers. Several possible explanations will be offered, and each discussed in turn.

1. There is a chemical weakening effect at ZPC, but the concentration range over which it occurs is extremely narrow. This seems highly unlikely. Researchers who do report chemically enhanced effects describe them as occurring over a concentration range of at least one order of magnitude above and below the ZPC concentration (*6, 30*).

2. This study has incorrectly determined ZPC values for the systems tested. It would seem that the good agreement previously cited between this research and results reported by others for the same systems negates this possibility. Furthermore, tests using aluminum chloride as a saturating fluid spanned the concentration range from $10^{-5}M$ to $10^{-2}M$, some three orders of magnitude. No statistically significant reduction in failure stress was observed in any of these tests.

3. Chemical weakening effects are only manifested at very slow strain rates, or over a long period of time with static loading. This remains very much a possibility. The latter set of conditions is consistent with the stress corrosion cracking mechanism suggested by Anderson and Grew (*18*). In addition, Ishido and Nishizawa (*7*) reported that while the development of microfractures was facilitated by a ZPC condition, an incubation period was nevertheless required. Dunning, Lewis, and Dunn (*30*) also found that the time to failure of sandstone cores under compression was related to zeta potential. On the other hand, the present investigation showed no difference in failure stress in samples tested at strain rates differing by an order of magnitude. The 14% reduction in failure stress seen in the water-saturated samples was achieved without a period of static loading.

4. Results of some researchers have been based on inadequate sampling or have not been subjected to proper statistical analysis. Many investigators have failed to be explicit in describing their data base or methods of statistical analysis. A notable exception is the work of Karfakis and Akram (*12*), who included Student's t test results in their publication. An insufficient data base coupled with large variations in the strength of geologic materials could account for the widely discrepant and sometimes irreproducible results reported in the literature.

5. A chemical weakening effect does exist, but it is so specific to certain combinations of minerals and solutions as to be of little general use. While this possibility exists, other explanations seem more plausible.

The last point to be discussed is the role of water. Additives, regardless of their nature, represent but an infinitesimal part of an aqueous solution. The water molecule itself is singular in many ways, e.g., large dipole moment, capable of hydrogen bonding, etc. Wetting of glass to reduce the stress necessary for fracture is a well-established laboratory practice. This is generally attributed to the adsorption of water, with a concomitant reduction in surface energy (*31*, p. 138). All tests described in this report showed a consistent 14% reduction in failure stress when the samples were saturated with an aqueous solution, regardless of the nature of the solute. For this reason, it is suggested that the observed stress reductions may be attributable to maximum adsorption of water, as opposed to any other chemical species present. Changes in the zeta potential of the system are an effect of this adsorption, and are not the cause of the reduced compressive strength. Unfortunately, confirmation of this mechanism is beyond the scope of the present investigation.

## CONCLUSIONS

Sandstone cores saturated with tap water or other aqueous solutions showed a consistent 14% reduction in failure stress under uniaxial compression compared with vacuum-dried cores tested in air. This investigation showed no evidence that this effect was enhanced by the presence of any other additive tested. No correlation was found between zeta potential and compressive strength. While the results of this study are specific to the material tested, they do suggest that similar results could be expected in engineering applications, such as the stress relief of sandstone roof or floor members.

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